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THE STUDY OF SINGLE CRYSTALS

for

SPACE PROCESSING AND THE EFFECT OF ZERO GRAVITY

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PAINE COLLEGE

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FOREWORD

The present report, No. PC-NAS-003, dated August, 1975, of Paine College, Augusta, Georgia, is the Final Report for NASA Grant NSG-8002, entitled, "Study of Single Crystals for Space Processing and the Effect of Zero Gravity." This report covers the period from January 15, 1975 till August 31, 1975.

The work reported herein was performed under the technical direction of Mr. Tommy C. Bannister, Space Sciences Laboratory, NASA/Marshall Space Flight Center, Huntsville, Alabama.

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ABSTRACT

A study was undertaken to analyze different growth techniques which may be affected by the space environment. The literature on crystal growth from melt, vapor phase and float zone has been reviewed and the physical phenomena important for crystal growth in zero-gravity environment has been analyzed. Recommendations have been made for potential areas of crystal growth feasible for future long-term NASA space missions. Also included herein, a bibliography of articles collected in the area of crystal growth in general. This study is not yet complete and needs further investigation in different areas of crystal growth not dealt with in this report.

INTRODUCTION

The promise shown by the results of the Skylab I & II experiments on material science as discussed and presented in a meeting¹, at NASA/Marshall Space Flight Center, Huntsville, Alabama, are in confirmation of the possibility of processing of materials in space on a routine basis. The materials can be processed for making efficient semiconductors for use in the field of communications, and materials which will make better super-conductors for the control and distribution of energy. The ASTP program will continue the activity begun on Skylab and multiply its effects. The future space shuttle and Spacelab will provide suitable flight capabilities for space processing when they become operational.

The capability of sounding rocket experiments involving weightlessness will soon be demonstrated in the FY1975. During this period, NASA is planning to run programs that have many analogies to the shuttle program itself.

II. OBJECTIVES

The objectives of this program are to study the mechanism of crystal growth which may be affected by the space environment and to deduce conclusions as to the relative technical and scientific advantages of different growth methods. To meet these objectives, the literature on crystal growth from melt, solution, vapor phase and float zone has been reviewed and the physical phenomena important for crystal growth in a zero-gravity environment has been analyzed.

In this report, the commonly used crystal growth techniques are mentioned and a review of melt growth and vapor phase processes in relation to the crystal growth in space environment are discussed. Also included herein is a bibliography of articles relevant to the physical phenomena and theory of crystal growth.

This work may be treated as a continuation of the work already reported in the annual report, PC-NAS-002, February, 1975.

III. Crystal Growth Processes Relevant to Space Environment

The crystal growth of solid state materials from melt, the vapor phase and the solution is an art of many years. The temperature profile in a crystal growth system is of great importance for understanding the transport and growth phenomena in general and for morphological stability in particular. In growth from melts, the role of interfacial temperature gradients, as well as temperature fluctuations, is rather well understood. A good deal of experimental data as well as proven theoretical models are available, relating compositional variations with growth rate fluctuations that are induced via natural or forced convective temperature instabilities.²⁻⁴ In solution growth, where the interfacial kinetics is in general more complex than growth from melts, it has been reported⁵, that short-term temperature instabilities of few millidegrees can lead to structural inhomogeneities, such as solvent occlusion. In crystal growth from vapor phase, comparably few investigators have been concerned with temperature distribution and fluctuation effects.

A thorough review on chemical vapor deposition (CVD) systems were put forward by Curtis and Dismukes⁶. Later, Rosenberger, et al⁷, reported, in detail, the heat transfer and temperature oscillations in CVD. The positive effects of micro-gravity on crystal growth and fundamental properties of the vapor transport reactions were established by analyzing the results of GeSe and GeTe vapor transport experiments performed on Skylab by Wiedemier, et al⁸.

IV. 1. Growth from the Melt

The crystal growth from the melt has been the most widely used method for the preparation of large single crystals. The most important common characteristic of this process is that some portion of the solid-liquid interface is in contact with the crucible. Any irregularities on the boat surface will affect the growth and may cause spurious nucleation. The material under consideration must melt congruently without irreversible decomposition, and there is no solid state phase transformation between the melting point and the temperature to which the crystal will be cooled later.

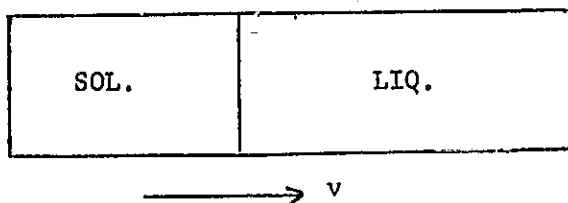
IV. 1.1 Principles of Melt Growth

In melt growth, we are mainly concerned with the controlled solidification of a melt in such a manner as to promote the extension of a single nucleus without the introduction of new nuclei and with minimum chemical and structural disorder in the crystal. To avoid forming new nuclei and to avoid instability in growth surface, which leads to chemical inhomogeneity in the doped crystal, extensive zones of super cooling in the melt must be avoided. The latent heat generated by solidification process must be removed by conduction into the solid rather than into the liquid. Directional solidifications must be achieved in which growth occurs onto part of the crystal whilst a heat sink is attached to the remainder. Consider a molten bar solidified by

passing a planar solid-liquid interface along it, normal to its axis at a velocity 'v' (figure 1). If the temperature gradients in solid and liquid at the interface are G_s and G_L , then the continuity of heat flux requires,

$$K_s G_s - K_L G_L = Lv$$

where K_s and K_L are the thermal conductivities of solid and liquid and L is the latent heat of solidification per unit volume.



(fig. No. 1)

If it is required that G_L is greater than 0, then clearly for $v > 0$, G_s must be greater than 0, and heat must be extracted from the growing crystal. This can occur by conduction down the crystal and radiation from the surface. In the melt, in addition to these mechanisms, convection will be important.

During the crystal growth by solidification of a melt, the crystal does not have exactly the same imperfection as the melt because of the segregation of impurities. In the case where only one impurity with a segregation coefficient k is present, the impurity distribution along the length of the crystal is given by,

$$C(x) = kC_0 (1-x)^{k-1}$$

where $C(x)$ is the concentration of impurity in the crystal as a

function of the fraction, x , of the melt solidified, and C_0 is the initial concentration of the impurity in the melt. Unless the segregation coefficient is near unity, the impurity content changes along the length of the crystal making it impossible to produce a crystal of uniform impurity distribution. Many articles^{9,10} deal with the melt growth in general in a greater detail.

IV. 1.2 Techniques

The various techniques of melt growths can be classified in two general headings:

- a) Normal freezing in which a molten charge is directionally solidified
- b) Zone melting in which a zone is melted in a solid ingot and then caused to pass along the ingot

The above techniques can be subdivided into the following categories:

- (a) Normal Freezing Techniques
 - i) Crystal pulling
 - ii) Pedestal growth
 - iii) Vertical Bridgeman/Stockbarger
 - iv) Kyropoulos
 - v) Verneuil
 - vi) Horizontal normal freeze (horizontal Bridgeman)
- (b) Zone Melting Techniques
 - i) Horizontal zone melting
 - ii) Float zone method

IV. 1.2a Normal Freezing Techniques

Earlier, in a conference on manufacturing in space, Utech¹¹, discussed, in detail, the possible mechanisms by which defects

can be introduced in a melt grown crystal. According to Utech (loc. cit) the mechanisms to account for the origin of dislocations in crystals grown from the melt are:

1. Introduction from the seed
2. Externally applied stresses
3. Stresses of thermal origin
4. Concentration gradients (thermal convection)
5. Condensation of vacancies
6. Trapping of inclusions

The results of the Skylab experiments^{12,13,14}, indicate that the possible causes (#2,3,4) are substantially eliminated in a zero-gravity environment. Of course, half of the mechanism (#1,5,6) still remain. But it seems unlikely that any of these can themselves account for large concentrations of dislocations and defects in the crystals. It was established by Witt, et al¹², that ideal diffusion controlled steady state conditions, never accomplished on earth, were achieved during the growth of Te-doped InSb crystals in Skylab. Surface tension effects were found to establish non-wetting conditions under which free surface solidification took place in confined geometry. In addition, it was possible, for the first time, to identify the origin of segregation discontinuities associated with facet growth, the mode of nucleation and propagation of rotational twin boundaries, and the specific effect of mechanical shock perturbations on segregation.

In another experiment¹³ on Skylab, single crystals prepared by seeded containerless solidification indicated that conditions of no-fluid-flow were established.

The results of Yee, et al¹⁴ on a directional solidification

of InSb-GaSb alloys on Skylab, demonstrates the following results:

The concentration profiles and compositional homogeneity were both strongly influenced by the magnitude and direction of 'g'. There was a great reduction in twinning brought about by space processing. Gas bubbles were more uniformly distributed in the space-processed ingots, which, of course, is not a very significant result, because they can be avoided by solidification in a reasonable vacuum.

IV. 1.2 b Zone Melting Techniques

While good quality single crystals of many electronic materials have been produced by the Czochralski technique from the melt contained in a crucible, the chemical reactivity of some molten materials has made it difficult to find a satisfactory crucible to contain the melt.

One of the unique advantages of zero-gravity environment for processing of materials is the elimination of containers in the handling of molten liquids. Three techniques have been developed to perform containerless melting on earth; the electromagnetic levitation of a liquid metal drops weighing 5 to 10 grams, the use of sessile drops which freeze onto a seed of similar composition as in Verneuil technique; and the use of molten floating zones suspended between cylindrical rods of the same material and contained by surface tension for heights less than 1 to 1.5 cm. Carruthers¹⁵ has studied the liquid floating zones on SL - IV, the third Skylab mission. However, zone melting may

be used as a single crystal growth technique and, indeed, single crystals often result when the technique is used for purification. It is, of course, an advantage of crystal growth by zone melting that control of impurities can usually be obtained at the same time.

Horizontal Zone Melting

Horizontal zone melting is basically the same as the horizontal Bridgeman method, except that a short furnace (frequently an r.f. coil) is used to melt a zone which is then moved slowly along the bar. The advantages of the method over the normal freeze process (Bridgeman) are: a) reduced contamination of the melt by the boat, b) less heater power required, and c) zone-refining for purification and zone levelling for uniform doping can be used.

Float Zone Method

Float zone process was first described by Keck and Golay¹⁶, and later independently by several others (Emeis¹⁷; Theuerer¹⁸). Its first application was to the purification of silicon. Surface tension holds a molten zone of liquid in a sample whose axis is vertical. Since it is a crucibleless technique, so the reactivity with the boat is no more a problem.

In the absence of a boat, rf coupling to the boat is not possible, so heating must be provided by direct coupling to the melt (provided it is conductive enough) or by radiant heating from a resistance heater or by focussing a radiant source. Some stirring may be affected by independently rotating the two ends of the sample in opposite directions.

The conditions for zone stability have been discussed by Heywang and Ziegler¹⁹ and Heywang²⁰. Later, Brice¹⁰, discussed, in detail, the stability of such zones. The major force holding a floating zone in place is surface tension, cohesion between the solid and liquid is usually negligible and levitation due to radio frequency fields is also usually small. If feed rod and crystal are of cylindrical cross-section, it is possible to equate the hydrostatic pressure and surface tension forces in various elements of a zone and hence, obtain information about the shape and stability of the zone.

Keck, et al²¹, showed that the maximum stable rod radius was,

$$r_{\max} = 0.92 (\gamma/\rho g)^{\frac{1}{2}}$$

where γ is the surface tension of the liquid, ρ is the density and

g is the gravitational constant.

Heywang²⁰ has shown that the agitation is one of zone length where the maximum length, ' L_{\max} ', is given by,

$$L_{\max} = 3.46r_0$$

for small rods, but for large rods,

$$L_{\max} = 2.84 (\gamma/\rho g)^{\frac{1}{2}}$$

Green²² gives a treatment which does not assume that the rods and zone surfaces have cylindrical symmetry. For cylindrical symmetry, his analysis gives:

$$L_{\max} = 2.62 (\gamma/\rho g)^{\frac{1}{2}}$$

Carruthers and Grasso^{23,24} have shown that under conditions of zero-gravity, the maximum stable zone length equaled the circumference. This was confirmed by the Skylab experiments.

Brice¹⁰ has given a list of materials grown by the floating zone method and is included in Table 1.

Table No. 1

(Brice¹⁰)

Materials Grown by Float Zone Method

Material	Melting point (C)
W	3400
VC _{0.8}	2700
HB ₂ , YB ₄	up to 2600
Mo	3500
MgAl ₂ O ₄	2050
Rh	1970
Y ₃ Al ₅ O ₁₂	1950
Zr	1860
Ti	1800
YFeO ₃	1720
Sr ₂ Nb ₂ O ₇	1700
BaTiO ₃	1600
Pd	1544

Table No. 1 (cont)

Fe	1554
Fe+3%Si	~1500
Ni	1455
Si	1430
Gd	1312
GaAs	1237
Ge+Si (< 3.2%)	~1200
Cu	1083
NaCl	801

Table No. 2 lists some of the difficulties with the floating zone method with possible remedies as given by Brice¹⁰.

Table No. 2

Symptoms	Possible cure
1. Zone unstable	a) Decrease length by concentrating heat input b) Ensure mechanical stability
2. Crystal striated	a) Ensure that power source is stable b) Ensure that movements are smooth
3. Crystal heavily dislocated	a) Take greater precautions with seal-on and necking b) Improve seed quality c) Spread heat input or add after heater
4. Constitutional super cooling	a) Increase temperature gradient b) Decrease growth rate c) Decrease solute concentration

According to Carruthers¹⁵, the use of zero-gravity environment removes some of the constraints imposed on the dimensions of floating zones, eliminates thermal convection and allows more extensive geometrical modifications than permitted on earth. The

Skylab experiments indicated the following results:

a) The maximum stable zone length recorded was 2.90 in and was thus in excess of the theoretical value (equal to the circumference) for a right circular cylinder.

b) It is necessary to have some idea of the transient spinup time required for the liquid zone to reach steady state rotation after discs have started to rotate. Momentum is transferred to the liquid at a speed of $(\nu\Omega)^{1/2}$ cm/sec, where ν is kinematic viscosity and Ω is the rotation rate. Thus, if the zone length is 'l', the spinup-time is approximately:

$$t \approx l / (\nu\Omega)^{1/2} \text{ sec}$$

A number of observations made on isorotated zones using air bubbles and rotation indicators showed that the results were in agreement with the above equation.

V. I. Growth from the Vapor Phase

Many semiconductors do not melt at temperatures and pressures conveniently obtained in the laboratory and have, in some cases, been successfully grown from the vapor phase. For this technique to be applicable, the material of interest must either vaporize without undergoing irreversible decomposition or be preparable by chemical reaction of gaseous reactants.

This technique has the distinct advantages that refractory materials can be prepared at temperatures considerably below their melting point or decomposition temperature, and that the impurity concentration and distribution in the product can be controlled to an extent not easily obtainable by other techniques.

The positive effects of micro-gravity on crystal growth and fundamental properties of vapor transport reactions were established by analyzing the results of GeSe and GeTe vapor transport experiments performed on Skylab as proposed by Wiedemeier, et al⁸.

Crystal growth studies without convective interference in a micro-gravity environment should yield fundamental data for vapor transport technique and reveal the inherent transport properties of a chemical system. Due to its inherent simplicity in terms of a defined solid-gas phase system, the vapor transport technique is well suited to observe micro-gravity effects and other unexpected phenomena.

V. I. 1 Chemical transport technique

The chemical transport technique is applicable to solid substances which will react reversibly with a gaseous reagent (the transport agent) to form volatile products²⁶. The vapor species migrate from the source to the condensation zone of the reaction vessel where, at different temperatures, a reverse reaction occurs with formation of the solid. The necessary concentration gradient is established by means of a temperature gradient. Under optimal experimental conditions, well defined single crystals are formed by the condensation reaction. The transport reaction is carried out in sealed evacuated tubes of fused silica which are subjected to the desired temperature gradient in a horizontal two-zone tubular resistance furnace.

The transport of species via the gas phase can be described by gravity-driven convection. In a gravitational field and in a temperature gradient, both transport modes occur simultaneously. It is a unique feature of the vapor transport technique to select experimental conditions such that one or the other mode can be predominant.

Nucleation control in vapor phase growth is usually a problem, especially when bulk crystals are desired. Epitaxial films may usually be grown without too much difficulty in nucleation control. This is because the thickness of the film required is not great, the growth rate may be slow, and the supersaturation need not be large enough to cause nucleation anywhere but on the substrate (seed). When bulk crystals are desired, growth rates must be higher, and homogeneous and wall nucleation becomes a

problem. Scholz and Kluckow²⁷, have shown that such nucleation can be greatly reduced in vapor growth by temperature cycling during growth.

V. I. 2 Advantages of vapor growth in profile control

Vapor growth presents several advantages in profile control.

a) The temperature can be low so that solid-state diffusion after growth will not alter as 'as grown' profile.

b) Concentration of dopants in the gas phase can be altered abruptly (if the dopants or their compounds are volatile), by simple expedients such as opening a valve or changing the temperature of the reservoir containing dopant.

c) Growth can be made quite slow and can enable one to grow differently doped material in different regions of the substrate, and the application of masks and their removal in various sequences could allow the preparation of elaborate three-dimensional arrays of single crystal material with complicated concentration profiles. Such techniques, where masking is used during diffusion process, are central to the preparation of monolithic circuits.

V. I. 3 Skylab Results (ref 8, 25)

The combined experimental evidence from the analysis of the space-grown crystals confirms the predicted positive effects of micro-gravity on crystal quality as exemplified by crystals of GeSe and GeTe.

The second major result of the Skylab experiment M556 is the observation of greater mass transport rates than expected in micro-gravity environment. This observation is of scientific and technological significance with respect to the theoretical extension of the conventional transport models and the possibility of growing higher quality crystals at reasonable rates by vapor transport techniques in future NASA missions.

VI. Effect of Zero-gravity on Crystal Growth Processes

Nearly all crystal growth processes involve both a solid and a fluid (liquid or vapor) component. Since internal bonding forces in solids are much greater than the 1-g forces, only the properties of fluids are, in general, influenced by the gravity. In the liquid state, intrinsic forces, such as cohesion and surface tension, are of the same order as 1-g forces. The familiar properties of liquids are the result of the interaction of the inter-molecular forces and the gravitational forces. In the absence of gravitational forces, the behavior of fluids will be governed by the molecular forces alone. Thus, the low-gravity conditions will have a significant role on the fluid behavior which will have pronounced affect on crystal growth processes. Grodzka, et al^{28,29}, have studied, in detail, the natural convection in low-gravity environment. On the basis of the Skylab results, the effect of zero-gravity on crystal growth processes are summarized below:

The experiment of InSb (ref 12) proved unambiguously the uniqueness of zero-gravity conditions for obtaining directly fundamental data on crystal growth and segregation associated with solidification. Ideal steady state growth and segregation (exclusively diffusion controlled) were achieved leading to three-dimensional chemical homogeneity on a micro scale over a macro scale dimension. Surface tension effects led to phenomena previously never observed and theoretically not predicted. In the absence of convective interference, it was possible to identify segrega-

tion discontinuities associated with facet growth and to explain their origin on the basis of spurious nucleation.

On the basis of another experiment on InSb (M-560) (ref 13), it was concluded that highly perfect single crystals can be prepared by seeded containerless solidification. Large single crystals could be prepared by this technique, which will be a unique advantage of low-gravity environment.

In vapor growth experiments (ref 25), in addition to the improved crystal quality, the major result was the observation of greater mass transport rates than expected in micro-gravity environment.

VII. Recommendations

The results of the Skylab experiments strongly suggest that the space environment can be uniquely utilized for processing of materials for a variety of purposes. The high vacuum associated with space, although convenient in many respects, is not considered to be of great consequence, since relatively high vacuums are available on earth at reasonable cost. So all the advantages of crystal growth in space revolve around low gravity environment.

There are some unique materials as discussed in the earlier report³⁰, which makes the crystal growth in space very attractive. In order to justifiably grow in space, such materials should probably meet the following requirements:

- a) Material deform easily and yet must be grown unsupported.
- b) Materials which cannot be grown in crucibles because of chemical reactions and yet needed for many devices.
- c) Materials with greatly reduced twinning. (The result was seen to be most exciting by the experiment of Yee, et al¹⁴ on the Skylab).
- d) Materials should be float zone refined, but have very low surface tensions and cannot be stabilized by electromagnetic suspension method.
- e) Materials for bubble memory devices.
- f) Intentional doping of materials which is completely diffusion controlled and eliminates the convective currents.

- g) Large single crystals for device purpose, which are not easily produced under normal conditions.

In view of the above requirements, the following methods of growth can be considered as potential areas which can be planned for future missions. Since the work on this project is not yet finalized it is difficult to analyze the whole area of crystal growth. Based on the results of the Skylab, the following comments can be made:

1. Float zone crucibleless crystal growth experiments. The use of a zero-gravity environment removes some of the constraints imposed by the dimensions of floating zones, eliminates thermal convection and allows more extensive geometrical modification than permitted on earth.

2. The growth of crystals by vapor transport. The results of Skylab confirm the unique conditions of weightlessness for material processing and for the observation of basic transport phenomena. The role of convection in the conventional chemical vapor epitaxial growth processes can be determined by experiments in space.

3. Steady state growth and segregation under zero-gravity. Production of homogeneously doped single crystals for device purposes. Determination of diffusion coefficients of common dopants in different host semiconductors.

4. Conventional melt-growth experiments by crystal pulling. To study the crystal perfection in Czochralski growth and investigation of melt shape in weightless crystal growth. Study and preparation of metals (ref 31).

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